

The Nature of the magnetism-promoting hole state in the prototype magnetic semiconductor GaAs: Mn

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Abstract

Recent experiments [1] suggest that the ferromagnetism (FM) in GaAs: Mn is determined by the impurity band rather than holes in the valence band. We discuss here the physical mechanism of FM mediated by the carriers in impurity band, where the Mn d-level play a crucial role. The theory is based on the first principle approach.

The paradigm system that combines ferromagnetism (FM) with semiconductority involves Mn⁽²⁺⁾ impurity ions substitution for Ga⁽³⁺⁾ atoms in GaAs [2, 3, 4, 5, 6, 7]. Such acceptor substitution creates a hole that interacts with the local moment of d⁵ Mn. This doping-induced magnetism could lead to electrical control of FM, to the potential benefit of spin-electronics (spintronics). The nature of the ferromagnetism, including its dependence on the hole concentration and on that of the Mn ions depends, however, on the physical nature of the hole state. One view -the "host like hole" model [2, 3, 4, 5] has been that the hole resides inside the GaAs valence band. Such view would permit the use of the language of GaAs semiconductor physics (s-p bonding, extended wave functions, RKKY exchange) in analyzing the ensuing magnetism and its dependence on concentration of the relevant species. This scenario, underlying most Model Hamiltonian treatments of the problem [3, 5], was inspired by the previously known case of isovalent Mn doping of CdTe, where, on account of the host metal atom Cd⁽²⁺⁾ having the same charge as the magnetic impurity ion Mn⁽²⁺⁾, hole formation required additional doping. Such doping was accomplished by conventional hydrogen-like dopants (extended wave function in the effective mass approximation), leading to the expected host-like hole behavior underlying delocalized, effective-mass dopants. The different, "Impurity

Band” view [6, 7] emerged from the assumption that Mn doping is unlikely to be hydrogen-like, as it introduces into GaAs a fundamentally new (d) orbital type, absent from the (s, p) host. Then it is not obvious *a priori*, whether the hole will carry the identity of the host or that of the impurity; electronic structure calculations were needed to make this judgment. First principles calculations [6, 7] have suggested that the hole resides in an impurity band above the host valence band. This view implies that the magnetism could not be described in the language of host semiconductor physics alone, but rather by that related to the localized d band of Mn, hybridized with t_2 states of the host. Understanding which of the two views of the nature of the hole state is correct is important for deciding the pertinent guidelines for optimization of spintronic devices fabricated from FM semiconductors.

Some experimental observables related to the GaAs:Mn system are not very sensitive to the nature of the hole state, and could be explained either way. Examples of such non-crucial experiments include effects reflecting predominantly the existence of local moments of Mn interacting with some background carriers in the Kohn-Luttinger s-p bands, including magneto-transport, magneto-optics, thermoelectrical effects and other phenomena related to itinerant rather than to localized carriers near the top of the valence band. Remarkably, however, a recent crucial experiment [1] seems to have settled this debate in favor of the Impurity Band view on the mechanism of FM ordering by measuring independently the net densities of holes and that of the Mn ions, showing that the Fermi level resides above the valence band, inside the impurity band and that the Curie temperature T_c is controlled by this position rather than by the density of nearly free carriers as in the host-like-hole view. A Cover Story [8] echoed this view. While explaining that “the compass is pointing in the direction of impurity band scenario”, this piece [8] expressed the concern that some experimental features demonstrated by the most metallic samples are unclear as to their compliance with a particular hole model. We point out here that there are fundamental model-independent reasons for assertion that the placement of the hole in an impurity band (above the host valence band) holds both in the Mn- dilute limit (on the insulating side) and in the high concentration limit $n_{Mn} > 0.1$ (on the metallic side).

- (i) The Mn-induced acceptor level in III-V semiconductors is a result of orbital hybridization leading to a deep acceptor-like impurity band, not effective-mass like: Studies of the chemical trends in transition metal (TM) doped III-V semiconductors in a dilute doping limit [9, 10] have shown that these trends are determined by the strong d-p hybridization between the d-orbitals of TM ion and the p-orbitals of its nearest anion neighbors. The ensuing states are determined by the relative location of the atomic 3d levels of TM ions and the center of gravity of the heavy hole valence band. This results in two types impurity-related states: the bonding, TM localized “Crystal Field Resonance” (CFR) and the antibonding state called “Dangling Bond Hybrid” (DBH), in which the TM d state hybridizes with the vacancy-like dangling bonds. (See figure 1.) The ferromagnetic spin

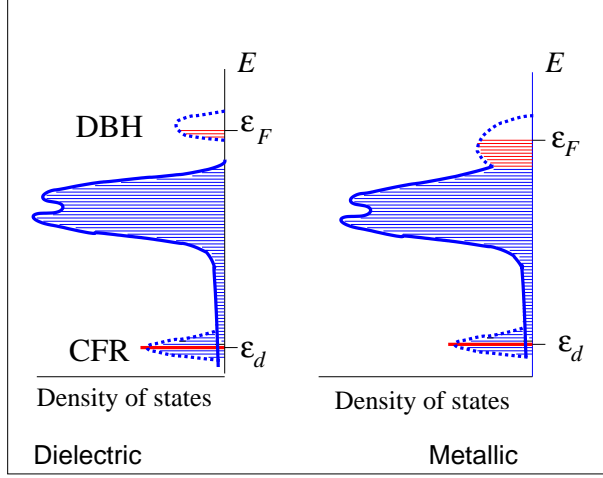


Figure 1: Density of electron states in dielectric (left) and metallic (right) phases of Ga(Mn)As. Two impurity-related peaks in DOS form a covalent pair CFR (related to the $\text{Mn}(d^5/d^4)$ level) - DBH (impurity band above the top of the valence band). Only the t2 partial contribution in the heavy hole band DOS is schematically shown. The CFR/DBH structure originated from the local dp bonding survives at any level of doping

arrangement leads to energy lowering (ground state) since more spins are occupying the bonding than the anti bonding state [6, 11]. In a given host semiconductor, the energetic positions of CFR and DBH vary in a universal way with the atomic number of the TM [6, 9, 10, 11]. On the other hand, considering different III-V semiconductors such as GaN-GaP-GaAs-GaSb with their valence band maximum (VBM) aligned according to their band offsets, the position of the DBH-CFR levels is approximately constant, as shown in references [6, 12]. These chemical trends unequivocally point to the d-p hybridization, rather than hydrogen-like acceptors, as the principal mechanism of formation of acceptor levels and impurity bands. Critically, Mn in GaAs, creates a DBH state outside the host valence band (inside the gap); the fact that this level is only 0.1 eV above the VBM should not be taken to imply that this is a shallow, host-like level, since its wave function is indeed composed from a multitude of \mathbf{k} -points (unlike effective-mass or $\mathbf{k} \cdot \mathbf{p}$ description) and contains d-character absent from the host crystal. In the more extreme case of Mn in GaN, where the CFR acceptor transition is very deep in the gap (1.4 eV above the VBM) and cannot possibly lead to ionizeable free holes, the magnetism clearly cannot be described by the host like hole s-d-exchange theory [13] with inter-site spin exchange. (See also discussion in [16]).

- (ii) The model of impurity potential used in the $\mathbf{k} \cdot \mathbf{p}$ approach to deduce a de-

localized nature of the Mn states is not appropriate for the 3d impurities: Ref. [13] attempted to describe Mn in GaAs as a square well potential interacting with the host bands; in the presence of many such wells the bound state) spreads out, creating the impression of a host-like resonance impurity state. This approach relies also on the RKKY mechanism to account for the FM, which was shown to be inadequate [14, 15]. The description of resonance impurity scattering by means of potential scattering [13] is misleading because it lacks the d-orbital nature of the real Mn state with its specific Mn d orbital energy. In turn, the d-p hybridization mechanism [(i) above] with its correct Mn d orbital energy places the state outside the host bands and is robust, in the sense that it cannot be significantly modified by any kind of screening, or disorder effects. In fact, disorder cannot destroy the local chemical bonds. The immediate consequence of this fact is that even for concentrated Mn, on the metallic side, where the impurity band is merged with the valence band and there is no gap for charge transport, the top of this impurity band is still formed by strongly hybridized d-p-orbitals (see Fig. 1).

- (iii) The impurity band picture correctly describes the dependence of T_c on the Fermi energy position: In accordance with above picture the Fermi level is pinned in the impurity band region of strong d-p hybridization both in insulating and metallic states. This impurity band modifies the host crystal density of states (DOS) generating a Lorentzian-like impurity band above the host valence band maximum. This DOS is responsible for the details of the hole-mediated Zener superexchange as shown in Refs. [16, 17].
- (iv) In GaAs:Mn films the Fermi level depends on the ratio between substitution and interstitial Mn-related defects, and the optimum concentration corresponds to half-filling of the impurity band. Thus, the dependence of T_c on the effective carrier concentration x has the 'dome-shaped' function observed in experiment (Ref. [1], Fig. 1). This type of dependence follows from the model calculations [16, 17] and first-principles supercell calculations [9] based on the mechanism of d-p-hybridized CFR-DBH states, and therefore on the pinning of these states to the universal energy scale (the valence band offset). A dome-like dependence $T_c(x)$ obtained within the model of impurity ferromagnetism due to Zener-like double exchange via the impurity band [16] can be seen in Fig. 2 of that paper.
- (v) Two recent experimental findings unambiguously support the statement that the d-p-hybridization is responsible not only for the Zener exchange but also for the shape of the DOS near the top of the valence band in metallic ferromagnetic GaMnAs. These are the dome-shaped $T_c(x)$ (Ref. [1] Fig. 1), and the absence of Drude peak in the infrared conductivity of "metallic" samples ([18], Fig. 10), ([19], Figs. 1 and 3), which indicates the absence of free charge carriers at the Fermi level in the samples.
- (vi) The mechanism of d-p hybridized hole states above the top of the valence

band provides guideline for optimization of devices fabricated from FM semiconductors: There are some important practical consequences of the change of FM model from host-like-hole to impurity band hole: (a) one should look for the fabrication and annealing regimes which favor the optimal half-filling of Mn-related impurity band; (b) the narrower is the band, the higher T_c is expected. To make this band narrower, the fabrication of heterostructures with spatially quantized impurity bands may be useful.

To conclude, we believe that the recent experimental findings together with the fundamental quantum-mechanical properties of Mn in III-V semiconductor hosts unambiguously point out on the localized nature of holes mediating the Zener exchange in GaMnAs .

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